

$$m = 5 K_c A F \quad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO_x (as NO₂) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO_x.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.

2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. *Analyst*. 104:837. September 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO _x), as NO ₂ , including:		
Nitric oxide (NO)	10102-43-9	ppmv
Nitrogen dioxide (NO ₂)	10102-44-07	

1.2 Applicability. This method applies to the measurement of NO_x emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_x (NO + NO₂) emissions are oxidized to NO₂ and NO₃. Then NO₃⁻ is reduced to NO₂⁻ with cadmium, and the NO₂⁻ is analyzed colorimetrically.

3.0 Definitions. [Reserved]

4.0 Interferences

Possible interferents are sulfur dioxides (SO₂) and ammonia (NH₃).

4.1 High concentrations of SO₂ could interfere because SO₂ consumes MnO₄ (as does NO_x) and, therefore, could reduce the NO_x collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal

with no control of SO₂ emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO₂ will reduce the MnO₄ concentration by only 5 percent if all the SO₂ is consumed in the first impinger.

4.2 Ammonia (NH₃) is slowly oxidized to NO₃⁻ by the absorbing solution. At 100 ppm NH₃ in the gas stream, an interference of 6 ppm NO_x (11 mg NO₂/m³) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH₃ injection to control NO_x emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of Section 16.0.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid (COOH)₂. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate (KMnO₄). Caustic, strong oxidizer. Avoid bodily contact with.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C-1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C-2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, Sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume

under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO_x from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (*e.g.*, a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225-t-05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.) from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm "M." Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO₂ Measurement Equipment. Same as in Method 3, Section 6.0.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.